Combustion Research Facility News

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N_2O photochemistry is studied using ion imaging technique

David Chandler and postdoctoral fellows David Neyer and Albert Heck, in collaboration with Steven Stolte, Maurice Janssen, and Wim Roeterdink of the Free University of Amsterdam, have recently finished a study of the unimolecular photochemistry of N_2O. The work was sponsored by the Chemical Sciences Division of the Office of Basic Energy Sciences of the Department of Energy.

When N_2O absorbs an ultraviolet photon, it breaks into a ground electronic state N_2 molecule possessing a significant amount of rotational energy and an oxygen atom in the excited $^1D_2$ state. N_2O is an important molecular species in combustion and an important photolytic source of $O(^1D_2)$ used for studies of kinetics and chemical dynamics.

> The photochemistry of N_2O is complicated by several factors.

The study of unimolecular reactions is critical to the understanding of both initiation processes in combustion as well as many bimolecular processes. When a radical attacks another molecule it may form a complex in which the initial energy is redistributed. The decomposition of the energized complex into products is a unimolecular dissociation process. Laser excitation may often be used to simulate chemical or thermal activation.

The technique of ion imaging was used to study the photochemistry of N_2O at ~200 nm. This technique relies on ionization of a photofragment by a laser pulse, in this case either the N_2 molecule or the oxygen atom. The ionized fragments are projected onto a light emitting screen and their positions are recorded. From analysis of the images the velocity of the fragments is obtained. Figures 1a and 1b show the images of the N_2 molecules that were produced in the ground vibrational level (v=0) and the J=64 and J=86 rotational levels, respectively.

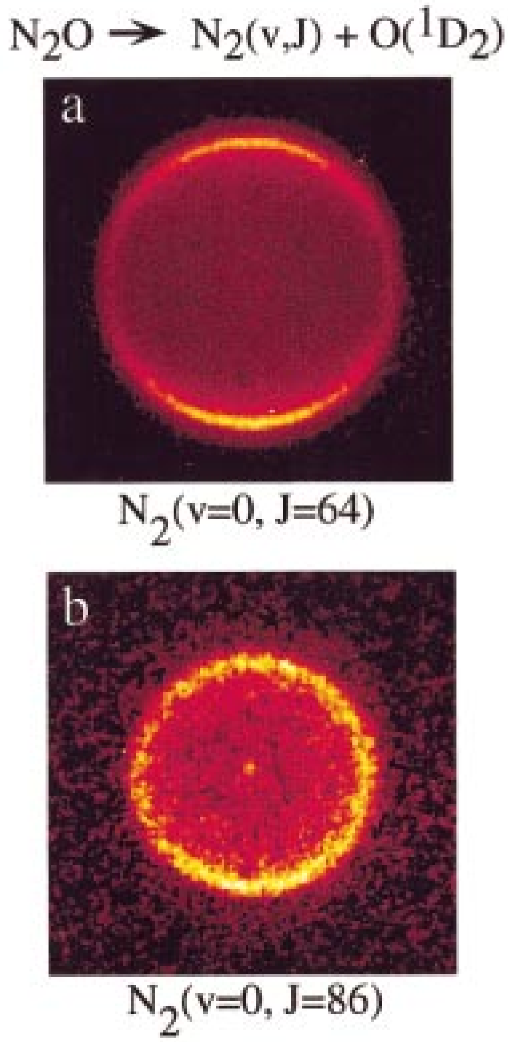
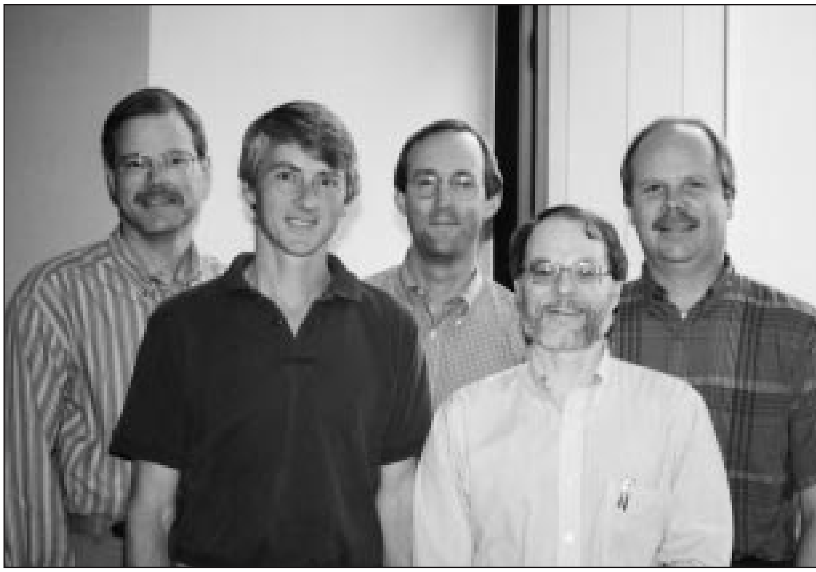


Figure 1. Ion images of N_2 photofragments obtained from the ~200 nm photodissociation of N_2O.

The photochemistry of N_2O is complicated by several factors. There are two possible electronic states that can be excited initially by the laser light, and as the molecule dissociates it undergoes a large geometry change. The ground electronic state is linear and the excited electronic states are bent.

From analysis of the N_2 and $O(^1D_2)$ atom images the team has determined the bending angle at which N_2O dissociates, which electronic states are produced by the initial excitation, and the velocity distribution of the $O(^1D_2)$ produced. This information is important for the validation of the potential energy surfaces of the excited states of N_2O as well as the interpretation of chemical dynamics experiments that utilize photolysis of N_2O as a source of $O(^1D_2)$ reactants.

Construction on the CRF Phase II project is on schedule (see *CRF News* **18**:5 and http://www.ca.sandia.gov/CRF/WhatsHot/WhatsHot.9702.html). Completion of the new office wing is forecast for late spring of this year. The configuration of this new space is designed to facilitate visitor programs focused on the modeling and simulation of combustion processes. A workshop focused on the interaction between experiment and computation in the development of predictive combustion models is being planned as the inaugural event for the new office complex. (See photo on Page 2.)

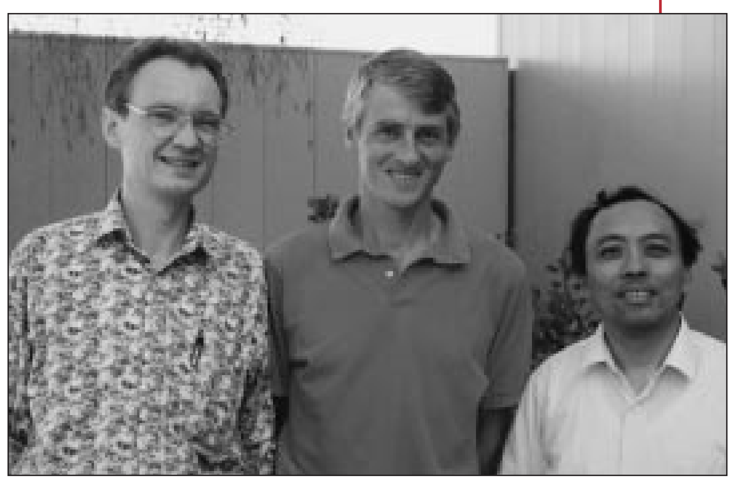


Five earn Employee Recognition Awards

Winners of the 1997 Sandia National Laboratories' Employee Recognition Awards from the Combustion Research Facility are (from left): Eric Rohlfing, Technical Excellence; Rob Barlow, Leadership; Mark Allendorf, Leadership; John Dec, Technical Excellence; and Duane Sunnarborg, Technical Excellence. The annual awards, given by Lockheed Martin, honor individuals and teams for outstanding service to Sandia and the nation.

Laura Ricart is a graduate student at the University of Wisconsin, Madison. She spent six months working with John Dec on adapting the University of Wisconsin version of the KIVA II code to match experimental results from the Sandia/Cummins single-cylinder research diesel engine.

The photo shows the new construction attached to Building 905, the office complex; laboratories are located in Building 906, hidden from view by the new wing.



(From left) Egon Hassel from the Technical University of Darmstadt, Germany completed a two-month visit, during which he collaborated with Rob Barlow and J.-Y. Chen (UC-Berkeley) on turbulent jet flame research and organizational aspects of the International Workshop on Measurement and Computation of Turbulent Nonpremixed Flames.

Understanding Cars, a movie made recently that includes footage of engines work at the CRF, will be shown on The Learning Channel on Saturday, May 10, at 7 p.m. (time may vary in your zone). The film crew spent a day with Pete Witze in his lab taking footage of his optically accessible engine in operation.

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Unburned fuel observed exiting piston-ring crevice in an engine

For contemporary automotive applications, engine designers are most concerned with all sources of unburned hydrocarbon (UHC) emissions during cold start operations and UHC emitted from combustion crevice volumes once the engine is warm. Using planar, laser-induced fluorescence (PLIF), Bob Green has observed the in-cylinder transport of unburned fuel that survives combustion in the propagating flame while trapped in the piston ring-land and ring-groove crevices.

By attaching an inclined mirror to the top of the piston in an optical-access engine, Bob was able to both (a) admit a laser sheet into the engine cylinder and (b) collect fluorescence emission from the plane of the sheet through the same window at the top of the combustion chamber. This allowed him to view the region near the top ring-land crevice opening when the piston was in the lower part of the cylinder without using a transparent cylinder.

The results reveal two distinctly different phenomena that occur depending upon the location of the top piston ring gap. At an azimuthal location well away from the ring gap, no UHC was detected during the expansion stroke, and an impulsively-driven wall jet, as illustrated in Figure 1, was observed exiting the crevice early in the exhaust stroke.

With the image plane located directly at the position of the ring gap, the UHC was observed being gently dispersed into a thin layer along the cylinder wall late in the expansion stroke and, during the exhaust stroke, this layer of UHC is scrolled into a 'roll-up' vortex that occupies the corner formed by the cylinder wall and the piston top as shown in Figure 2.

Whether the UHC exits the crevice as a wall jet or a wall layer, the results of this work show that late in the exhaust stroke, the strong flowfield driven by the roll-up vortex thoroughly mixes the UHC with the combustion products in the clearance volume above the piston, and this mixture then flows out the exhaust valve as the piston approaches the top to its stroke.

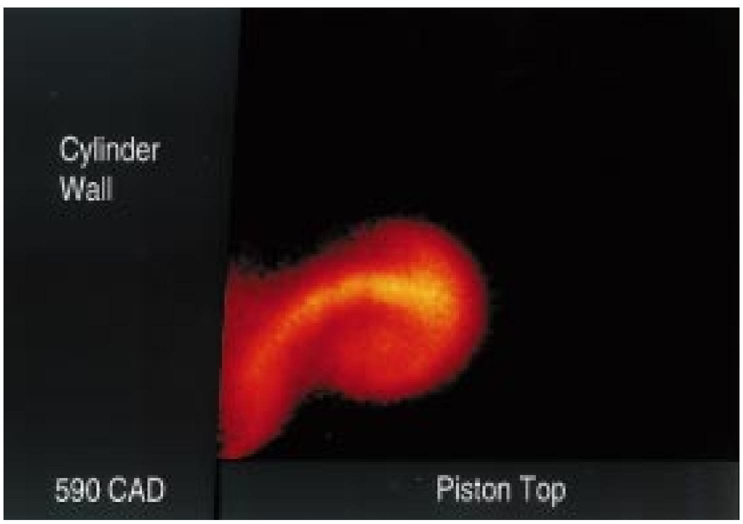

Figure 1. PLIF image of the evolution of UHC from the top ring-land crevice with the ring gap located well away from the image-plane.

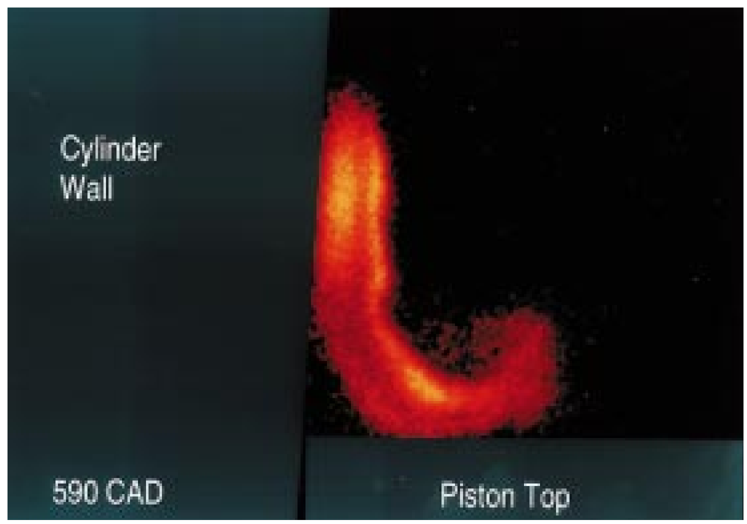

Figure 2. PLIF image of the evolution of UHC from the top ring-land crevice with the ring gap located at the image-plane.

CRF named to lead national Diesel Combustion Collaboratory

The Combustion Research Facility was recently named to lead a pilot project entitled the Diesel Combustion Collaboratory (DCC) under the auspices of DOE 2000. The vision of DOE 2000 is to accelerate the ability of the Department of Energy to accomplish its mission through advanced computing and collaboration technologies. In the CRF, there is currently a cooperative research and development agreement between Sandia, Los Alamos, and Lawrence Livermore National Laboratories and the major U.S. heavy-duty diesel engine companies, Cummins, Caterpillar, and Detroit Diesel.

A collaboratory is a laboratory without walls that enables scientists and engineers to carry out cooperative research independent of geography. The primary focus of the DCC will be the intensive integration of experimental results and computational modeling for application to advanced diesel engines that will meet more stringent emission regulations while maintaining or improving fuel efficiency. Lawrence Berkeley National Laboratory and the University of Wisconsin are also members of the DCC.

Sandia National Laboratories, a prime contractor to the U.S. Department of Energy, is operated by Sandia Corporation, a wholly owned subsidiary of the Lockheed Martin Corporation.

Air toxics program completed

In a three-year study concluded in December in the Burner Engineering Research Laboratory (BERL), a team consisting of Neal Fornaciari, Pete Walsh, Lloyd Claytor, Chris Edwards and Philippe Goix (Stanford), Rodney Sepulveda, Jim Boehmke, John Wirdzek, and Jim Alvarez showed that current refinery furnace hardware is sufficient to meet the 1990 Clean Air Act amendments.

Oil companies burn refinery fuel gas to heat crude oil for processing, thus are required to comply with the amendments, which regulate 189 air toxics. Any facility emitting more than 10 tons per year of one, or a total of 25 tons per year of any combination of these substances would be defined as a "major source" and required to implement "maximum achievable control technologies." The expense of such remediation might have rendered U.S. refineries unable to compete globally.

Whether refineries could keep emissions below requirements of the 1990 Clean Air Act amendments was unclear based on emissions measurements taken in the field. Using BERL allowed control over operating conditions so the measurements were reliable, providing insight into fluid mechanics and air toxics formation in the burners. Conditions that were varied during the program included firing rate, excess air, and fuel composition; 51 different operating conditions were studied. The BERL burned simulated refinery fuel gas, a mixture of methane, propane, and hydrogen, which is normally produced as a byproduct of petroleum processing.

"What we found was that if you operate your burner properly, air toxics aren't emitted," Neal said. "That's good for the refinery industry, because instead of needing new

burners or after-treatment equipment, they can just operate properly and not have emissions problems. We found that refinery fuel gas is as clean burning as natural gas, and we helped show that as long as burners are properly adjusted, no changes would be needed."

The DOE / Office of Industrial Technologies-sponsored effort included industry partners from Amoco, Chevron, the Gas Research Institute, Mobil, Shell, the Southern California Gas Company, and Texaco. Sandia and Lawrence Livermore National Laboratories provided chemical kinetics modeling, and the University of California / Los Angeles and Stanford University made reduced-scale experimental measurements. Energy and Environmental Research Corp. made the BERL emissions measurements. (See *CRF News* **15**:1, **16**:2, **17**:6, and **18**:6.)

Denise Swink, DOE Deputy Assistant Secretary in charge of the Office of Industrial Technologies, calls the $6 million program an ideal example of National Laboratory / industry collaboration.

The Second International Workshop on Measurement and Computation of Turbulent Nonpremixed Flames will be hosted by the Technical University of Darmstadt and held on June 3-4, 1997 in Heppenheim, Germany. Information is available through the Web site (http: / / www.ca.sandia.gov / tdf / Workshop.html).

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